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Modelling the carbonate system to adequately quantify ocean acidification

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Introduction

The ecological impact of ocean acidification resulting from the marine uptake of anthropogenic emission of carbon dioxide (CO_2) is attracting significant research effort, and the current scientific consensus is that ocean acidification poses a serious threat to the integrity of the marine ecosystem, key element cycles, biodiversity and the provision of goods and services to nation states (Caldeira and Wickett, 2003; Royal Society, 2005; Stern, 2006). There is little doubt that on-going ocean acidification and related changes in ocean carbonate chemistry will contribute to major changes in marine ecosystems, but we are only beginning to understand the mechanistic background, the diversity of sensitivities and the evolutionary consequences of its impacts (Feely *et al.*, 2009).

Ecosystem evolution over the next decades will be driven by factors including climate change, modification to fishing pressures, pollution and eutrophication. Marine system responses to ocean acidification are complex and involve several mechanisms that impact a variety of marine processes and trophic interactions. Therefore, the effects of ocean acidification need to be considered in the context of interactions with these other pressures. A policy relevant ecosystem approach to ocean acidification requires a synergistic consideration of both the complexity of drivers and the complexity of responses. This poses a significant challenge to existing model systems.

The use of coupled carbon cycle-climate models incorporating relevant parameters of natural variability alongside climate change parameters will be important for determining how regional and seasonal variations in factors such as CO_2 air-sea fluxes, temperature, salinity, ventilation and upwelling will cause changes in ocean carbonate chemistry (Garrard *et al.*, 2013). However, current ecosystem models are not yet able to adequately describe these processes, particularly in regional seas where a variety of complex interactions and feedback mechanisms complicate the situation further. This report reviews the current state of the art for describing the carbonate system in regional seas and examines the options for including an explicit representation of the carbonate system in the JRC Water Resources Unit marine models for the European Seas.

The Marine Carbonate System

Ocean acidification is related to the input of anthropogenic CO_2 to surface oceans from the atmosphere, leading to shifts in carbon chemistry that can cause changes to rates and fates of primary production and calcification of marine organisms and communities (Fabry *et al.*, 2008; Rost *et al.*, 2008). Present day atmospheric CO_2 concentration is the result of the dynamical equilibrium between anthropogenic emissions from fossil fuels (Boden *et al.*, 2011) and natural sinks from terrestrial and oceanic components (Falkowski *et al.*, 2000). CO_2 exchange between the atmosphere and the ocean is a critical process of the natural global carbon cycle, but increasing atmospheric CO_2 concentrations throughout the industrial era has led to a disruption in the carbonate system resulting in, among other changes, an unprecedented acceleration in falling pH levels (Caldeira and Wickett, 2003).

Oceans are a significant sink for anthropogenic CO_2, having absorbed ~30 % of total anthropogenic CO_2 emissions since the industrial revolution (Sabine, 2004). This has led in turn to a 0.1 pH unit reduction (equal to a 30 % increase in $[H^+]$, hydrogen ion concentration) since pre-industrial times (Caldeira and Wickett, 2003). It is the fast rate of change in atmospheric CO_2, unprecedented at least during the last 22,000 years (Joos and Spahni, 2008), that is the major cause for concern. Modelling studies indicate a further decrease of about 0.3–0.4 pH units in global ocean surface pH by 2100, depending on future CO_2 emissions (Feely *et al.*, 2009; Orr *et al.*, 2005; Caldeira and Wickett, 2003), corresponding to a decrease of about 45–50 % of carbonate ion concentration. This is beyond the range of natural variability and represents a level probably not experienced for at least hundreds of thousands of years, possibly longer (Caldeira and Wickett, 2003).

Historically, there have been large changes in the levels of atmospheric CO_2. For example, four hundred million years ago, before land was colonised by forests, CO_2 levels were probably 20 times higher (Royal Society, 2005). During slow natural changes, interaction with sediments rich in calcium carbonate ($CaCO_3$) tends to buffer the seawater chemistry. Due to this buffering process, the average surface ocean pH has not been much lower than about 8.2 for millions of years, even though there have been significant changes in atmospheric CO_2 concentrations (Royal Society, 2005). However, the current rate of change

in atmospheric CO_2 concentrations is at least 100 times higher than the maximum rates seen in ice core (IPCC, 2001) and proxy reconstructions (Pearson and Palmer, 2000). It will take tens of thousands of years for the changes in ocean chemistry to be buffered through neutralisation by calcium carbonate sediments (Archer and Brovkin, 2008; Ridgwell and Zeebe, 2005) though the level at which ocean pCO_2 will eventually stabilize will be lower than it currently is (Archer and Brovkin, 2008; Ridgwell and Zeebe, 2005).

Estimates of future atmospheric and oceanic CO_2 concentrations, based on the Intergovernmental Panel on Climate Change (IPCC) CO_2 emission scenarios and general circulation models, indicate a decrease in surface water pH of ~0.4 by the end of the century and a corresponding 50 % decrease in carbonate ion concentration (Orr *et al.*, 2005). This is supported by several long term observational data sets, such as the Hawaiian Ocean Time series (HOT/ALOHA, Dore *et al.*, 2009), the Bermuda Atlantic Time series Studies (BATS, Bates, 2007; Lomas *et al.*, 2013) and the European Station for Time Series in the Ocean (ESTOC, Santana, 2007), where a consistent decrease of about 0.02 pH units has been observed over the last 20 years. These rapid changes are likely to significantly reduce the natural processes that have buffered changes in ocean chemistry over most of geological time, with potentially serious consequences for the the multifaceted economies that currently depend on marine ecosystems (Royal Society, 2005).

Carbonate system equations

Four analytically determinable variables describe the carbonate system (Dickson *et al.*, 2007): dissolved inorganic carbon (DIC), partial pressure of CO_2 (pCO_2), pH and total alkalinity (A_T). Knowledge of any two of these along with basic physical properties is sufficient to derive the other two and the carbonate saturation state. DIC is the sum of the concentrations of the carbonate species:

$$DIC = \left[CO_2^*\right] + \left[HCO_3^-\right] + \left[CO_3^{2-}\right]$$

Currently, ~1 % of DIC remains in the form of dissolved CO_2 (including tiny amounts of carbonic acid, H_2CO_3 – the combination of these terms is given as CO_2^*), while the rest is in the form of bicarbonate ions (HCO_3^- , ~90 %) or carbonate ions (CO_3^{2-} , ~ 9 %). The abundances of each of the forms of DIC vary with temperature, salinity and pressure, and reflect the pH of the water. Alkalinity is approximately the sum of weakly bound negatively charged ions including CO_3^{2-} and HCO_3^- . The concentration of H+ (in mol·kg^{-1} seawater) approximates its activity and determines the acidity of the solution. Acidity is commonly expressed on a logarithmic scale as pH:

$$pH = -\log_{10}\left[H^+\right]$$

The marine carbonate equations are given by:

$$CO_{2(atm)} \Leftrightarrow CO_{2(aq)} + H_2O \Leftrightarrow H_2CO_{3(aq)} \Leftrightarrow H^+ + HCO_{3(aq)}^- \Leftrightarrow 2H^+ + CO_{3(aq)}^{2-}$$
$$CO_2 + H_2O + CO_3^{2-} \Leftrightarrow 2HCO_3^-$$

As the atmospheric concentration of CO_2 increases, the flux of this gas into the surface ocean will also increase following Henry's law. When CO_2 is taken up by the ocean, the first equation is driven to the right, lowering pH. CO_2 also reacts with CO_3^{2-} in seawater to form two bicarbonate ions. The resulting overall change is a decrease in carbonate and pH. With increasing atmospheric *p*CO_2, DIC increases and the equilibrium of the carbonate system shifts to higher CO_2 and HCO_3^- levels, while CO_3^{2-} concentration and pH decrease. The process is moderated by the alkalinity content of seawater. It is known as *ocean acidification* because, even though the surface waters will remain alkaline, seawater pH is declining.

There is a critical concentration of CO_3^{2-} ions below which calcium carbonate ($CaCO_3$) will start to dissolve. $CaCO_3$ solubility increases with decreasing temperature and increasing pressure, and a 'saturation horizon' is defined, the depth above which seawater is super-saturated and $CaCO_3$ will tend to be preserved, and below which seawater is under-

saturated. At present, most surface waters are substantially super-saturated and carbonate minerals tend to be preserved. In contrast, much of the deep ocean is under-saturated, creating conditions under which mineral forms of $CaCO_3$ are chemically dissolved. $CaCO_3$ exists in two commonly occurring forms: aragonite and calcite. The aragonite form of $CaCO_3$ is more soluble than calcite, so the aragonite saturation horizon is always nearer the surface than the calcite saturation horizon. Saturation state (Ω) is also affected by the production and remineralisation of organic carbon in coastal ocean water and sediments (Andersson, 2006), which in turn depends on inputs of nitrogen, phosphorus and organic carbon to the surface ocean water.

Acidification and decreasing $CaCO_3$ production have several consequences for the ocean carbon cycle. Production of $CaCO_3$ removes twice as much alkalinity as it does CO_2 from seawater (Frankignoulle *et al.*, 1994) so that decreasing $CaCO_3$ leads to elevated pCO_2 and a negative feedback with the atmosphere. On the other hand, the ratio of $CaCO_3$ to particulate organic carbon in sinking organic matter will decline (Archer, 1991) leading to a reduction in carbon export flux to the deep ocean.

Regions of high natural variability

There is natural spatial and temporal variability in carbonate chemistry across the oceans. Surface oceans have an average pH globally of about 8.2, but carbonate parameters will vary regionally (Steinacher *et al.*, 2009), seasonally (McNeil and Matear, 2008), with latitude (Orr *et al.*, 2005), with depth (Caldeira and Wickett, 2003) and with habitat (Striegl *et al.*, 2007), although the primary influencing factors are temperature and upwelling (Royal Society, 2005). These effects impose regional differences in carbonate chemistry (Steinacher *et al.*, 2009); for example the shallowing of carbonate saturation horizons towards the poles (Orr *et al.*, 2005) or the upwelling of CO_2 rich and under saturated water onto western boundary shelf systems (Feely *et al.*, 2008).

Thermal effects play a considerable role in driving the seasonal variation in surface pCO_2, particularly in the subtropics (Takahashi *et al.*, 2002). Temperature change affects both the rates of biological calcification as well as primary production and the chemical state of the

carbonate system in water. Warming a surface water parcel by 1˚C, without any other changes in salinity, DIC, or alkalinity levels, results in an increase in pCO_2 of ~4 % for water in equilibrium with a present-day atmosphere of about 370 atm (Takahashi *et al.*, 1993). Coastal upwelling systems consistently experience natural ranges in surface seawater CO_2 concentrations and pH that are among the most extreme in the ocean (Capone and Hutchins, 2013). Upwelling, older, deeper water carries high levels of CO_2, the biogeochemical imprint of accumulated microbial respiration of organic matter, to the surface. As a result, CO_2 levels in surface sea water in upwelling zones can exceed 1000 parts per million (ppm) and pH can drop as low as 7.6–7.7 (Feely *et al.*, 2008).

There may be high spatial and temporal variability shelf seas and reef systems (Blackford and Gilbert, 2007; Santos *et al.*, 2011; Thomas *et al.*, 2004) as a result of several concurrent processes. Primary productivity is often high in these areas leading to a large drawdown of DIC and consequent rise of pH (Thomas *et al.*, 2005a). In shallow regions, benthic processes can also significantly affect the pelagic carbon cycle and alkalinity (Thomas *et al.*, 2009). Terrestrial inputs, in particular from rivers, can also inject significant loads of DIC and total akalinity (A_T) into coastal systems strongly driving the carbonate system (Borges and Gypens, 2010; Gypens *et al.*, 2011), with highly productive shelf and coastal environments producing variations of as much as 1 pH unit (pH 7.5 – 8.5), according to Hinga (2002). Hypoxia in shallow regions leads to even lower pH levels due to the production of CO_2 by heterotrophic degradation of organic matter (Melzner *et al.*, 2012).

While much of the uptake of CO_2 takes place in the open ocean (Schuster and Watson, 2007; Takahashi *et al.*, 2002), continental shelves play a significant role through the mechanism of the shelf sea carbon pump. The continental shelf pump was originally proposed by Tsunogai *et al.* (1999) in the context of the East China Sea to describe the mechanisms that transfer carbon from the atmosphere via the continental shelf to the deep ocean, but this process has also been observed in the North Sea (Thomas *et al.*, 2004; Bozec *et al.*, 2005) and most mid- and high-latitude shelves have been recognized to be significant sinks for atmospheric CO_2 (Chen and Borges, 2009). Frankignoulle and Borges (2001) estimate that the north west European continental shelf takes up an additional ~45 % of CO_2 from the atmosphere compared to the fluxes proposed by Takahashi *et al.* (1995) for the

open North Atlantic Ocean. Globally extrapolated, the net uptake of CO_2 by coastal and marginal seas is about 20 % of the world ocean's uptake of anthropogenic CO_2 (Thomas *et al.*, 2004).

Interaction with other climate and anthropogenic drivers

The chemical changes resulting from the uptake of anthropogenic CO_2 by the ocean are well understood (Zeebe and Wolf-Gladrow, 2001), but predicting the response of these changes on marine biology, ecosystems and biogeochemical cycles is at a very early stage (for example, Blackford and Gilbert, 2007; Bourret *et al.*, 2007). There are both positive and negative effects and feedback mechanisms in response to high CO_2. Experimental exposures of organisms to ocean acidification conditions indicate a high level of variation in species' ability to accommodate these alterations, and other studies have found that changes in temperature and eutrophication have had a bigger effect on the ecosystem than ocean acidification alone (Hendriks *et al.*, 2010). It may even be that in some regions, other drivers are more important than ocean acidification to the carbonate chemistry: Borges and Gypens (2010) found that carbonate chemistry in the coastal zone responds more strongly to eutrophication than ocean acidification.

Even if other drivers do not mask acidification effects, they may play a significant role in their seasonal and interannual variability: Dore *et al.* (2009) showed that physical and biogeochemical processes alter acidification rates with both depth and time. Increasing levels of atmospheric CO_2 are also driving ocean warming (Meehl *et al.*, 2007), however predicting the combined effects of warming and acidification is difficult, as warming could either offset the effects of ocean acidification (McCulloch *et al.*, 2012) or aggravate it through an accumulation of stress effects (Anthony *et al.*, 2008). It is most likely to be the interactive effect of acidification and other direct or indirect results of global change that determines the effect of ocean acidification on marine organisms (Hendriks *et al.*, 2010). The dynamics of DIC in the marine systems are a combination of physical processes, carbonate chemistry and biological processes each operating on different scales, but observational data sets that characterise this range are rare.

On one hand increasing CO2 may lead to enhanced phytoplankton growth. On the other hand lowering of pH may have negative impacts on the health and reproduction of a wider range of marine organisms, for example, plankton, calcareous organisms and fish larvae. Experimental evidence on impacts is often contradictory, further complicating the ability to predict future effects. Many organisms, particularly those in extreme coastal environments are adapted to large pH ranges and are likely only to be affected once the pH ranges exceeds their natural tolerance.

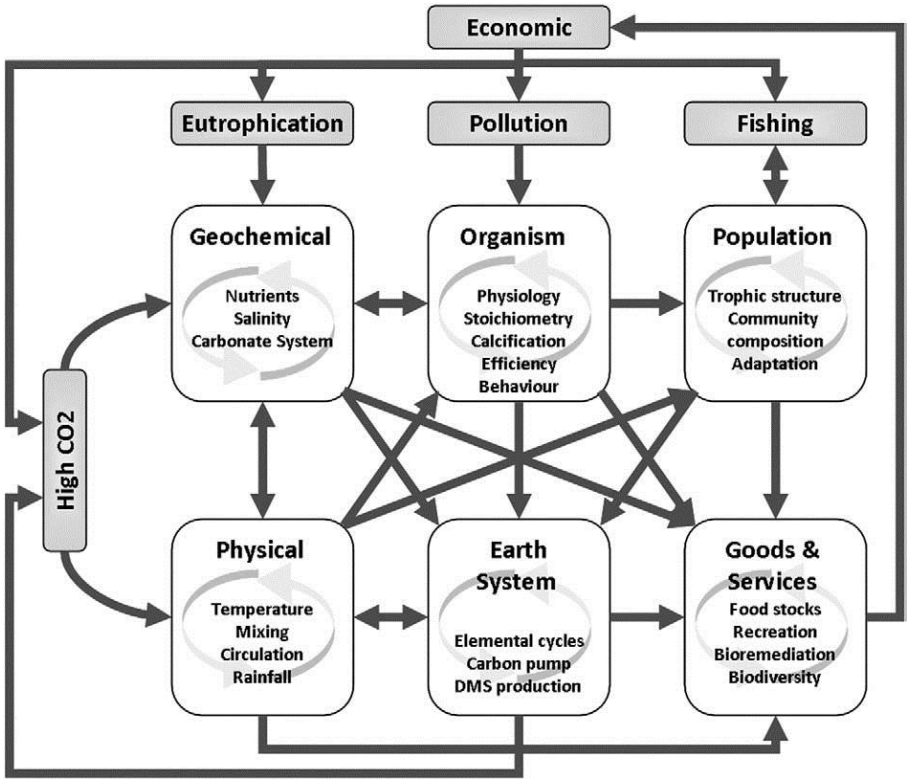

Figure 1: Some of the drivers, impacts and scales of organisation relevant to predicting ecosystem response to high CO2, from Blackford (2010). Drivers are indicated by the small shaded boxes and the scales of organisation by the large boxes. Selected impacts are listed within each box.

Due to these complex interactions, it has been difficult to provide sound scientific input regarding the expected environmental, social and economic consequences of ocean acidification (Garrard *et al.*, 2013). Blackford (2010) suggest that the sensitivity of ocean acidification to climate and anthropogenic drivers (such as those in Figure 1), and the complexity of their impacts on the ecosystem, points strongly towards a modelling approach for investigating the present and future states of the marine environment. Modelling approaches provide the possibility to investigate how changes in processes may interact,

but need a significant, multivariate body of observations to enable robust evaluation of regional models.

Existing models

There are two aspects to determining the carbonate system in marine models. Firstly the calculation of the partition of CO_2 within the carbonate system and secondly the calculation of the rate of exchange of CO_2 across the air-sea interface.

As described above, four master variables define the carbonate system: DIC, A_T, pCO_2 and pH. Knowledge of any two of these along with basic physical sea water properties (temperature, salinity, pressure) is sufficient to derive the other two, along with the carbonate saturation state (Ω), HCO_3^- and CO_3^{2-} (see Dickson *et al.*, 2007, for a comprehensive derivation). Typically, models use calculated DIC and a parameterisation of total alkalinity to drive the carbonate equations and derive pH and pCO_2.

Global scale models

There has been some progress with modelling carbonate chemistry at a global scale. An in-depth review of global scale models is omitted here as this type of modelling is not currently undertaken in the Water Resources Unit, but two methods are highlighted below. Subroutines from the first method could potentially be incorporated in a regional sea model (albeit with significant development). The second method is included since the potential complexity of an ecosystem approach to ocean acidification suggests that existing tools are limited in their utility for policy, eco- or earth-system questions and that new modelling approaches including a hierarchy of simple and complex models and novel model paradigms are required. This is an interesting approach, but it would require significant time resource and a modeller with the relevant experience with developing these types of models to introduce this at JRC. However, it may be an important approach to consider in order to deal with the issue of acclimation of species to ocean acidification.

A fast non-iterative compact scheme for calculating carbonate chemistry

Follows *el al.* (2006) obtain a fast, efficient and compact scheme for calculating the local carbonate chemistry with a simple method that does not require iterative methods. The accuracy of the scheme appears to be sufficient for coarse resolution global models, but it is unclear whether this method would be suitable for higher resolution shelf sea models, particularly those driven with synoptic physical forcing. Also, their method uses a parameterization for the total alkalinity, which although appropriate for the open ocean, does not hold for heterogeneous shelf environments (the issues of deriving this for shelf seas are discussed in further detail below).

An emergent ecosystem model

Follows *et al.* (2007) developed a marine ecosystem model where the microbial community "emerges" from a large number of potentially viable phytoplankton types with stochastically determined physiological characteristics (rather than from an explicit representation of functional groups of phytoplankton, like the biogeochemical models more familiar to our group). They suggest that this system mimics natural selection and is flexible enough to respond to changing ocean environments. In this way, their model can be used to interpret the structure and development of marine microbial communities, thereby revealing links between marine ecosystem structure, global biogeochemical cycles and climate change. Their emergent phytoplankton populations were in agreement with observed large-scale oceanic patterns in the distribution of phytoplankton biomass and community structure. The Follows *et al.* (2007) model has been used to describe patterns of diversity in phytoplankton (Barton *et al.*, 2010), and the interplay between ecology and biochemical cycles (Dutkiewicz *et al.*, 2009). This 'Darwinian' type of modelling takes a large step towards addressing the issue of inconsistent responses between species of similar functionality and the potential for acclimation and adaptation of at least some of the biological system with respect to ocean acidification, which will not be addressed in the 'Newtonian' approach typified by structurally fixed functional group models such as those run here. However, it is unclear at this stage whether this model would be suitable for

regional scale modelling as on global scales, few if any marine system models adequately represent the spatial patterns of production under present conditions. This would also require someone with different expertise to the marine modellers currently working in the Water Resources Unit.

Shelf sea models

Global marine, earth system or simple box models can describe broad scale phenomena, such as the relative vulnerability of polar ecosystems to under saturation (Orr *et al.*, 2005), but they lack definition in shelf sea regions, where a proportionally large amount of global productivity and human-ocean interactions occur. Models designed for use in coastal/shelf seas have the potential to improve over open ocean models through their enhanced resolution and improved process representation, for example, through the inclusion of tidal mixing, improved topographic representation by terrain-following vertical coordinates and more realistic terrestrial boundary conditions.

The primary uncertainties in modelling spatial and temporal variability in the carbonate system and accurately predicting ocean acidification relate to coastal and shelf environments and their boundaries (Blackford, 2010). The heterogeneity of shelf systems can lead to large spatial and temporal variations in the carbonate system and understanding the integrative effects of several drivers (such as, ocean acidification, temperature, surface fluxes, transport, light, mixing, species interactions, fishing, eutrophication and pollution) is necessary to evaluate ecological status in these societally important ecosystems.

A variety of models have been used to describe the carbonate system in shelf seas. Models that consider the carbon cycle study more particularly the phytoplankton and bacteria production (Allen *et al.*, 2002; Baretta *et al.*, 1995), but do not take into account the physical pump of carbon. Models of phytoplankton dynamics range from multi-component models with a single element limitation (Chai *et al.*, 2000; Kantha, 2004) to complex multi-element limitation models (Moore *et al.*, 2002). Denman *et al.* (2006) coupled an ecosystem carbon model to an inorganic carbon model with prognostic variables: dissolved inorganic carbon, particulate inorganic carbon, pCO_2 and alkalinity. In this case coupling between the organic

carbon and inorganic carbon compartments is realised through source and sink terms for the total inorganic carbon. For nitrogen-based models (Kantha, 2004), the ecosystem carbon cycle is coupled to the nitrogen cycle through constant C:N ratios or primary production.

The close coupling of the benthic system and euphotic zone in shelf systems increases the significance of processes such as the cycling rate of carbon through the benthos, the balance between benthic respiration and burial, the short-term buffering capacity of the sediments and the direct effect of acidification on the benthic system (Blackford, 2010). None of these processes are relevant in the open ocean, and this makes modelling the carbonate cycle in regional seas a much more complex task. Thomas *et al.* (2009) demonstrated the significance of anaerobically generated alkalinity in the North Sea and estimated that this process could be responsible for up to 60 % of carbon uptake in marginal seas. Nutrient and light-driven biological processes impart a distinct seasonality on the shelf carbonate system, which in return is sensitive to changes in phenology and distribution of production noted by several researchers (for example, Beaugrand, 2004).

Of the models described below, ERGOM is already used successfully in the Water Resources Unit (albeit without any of the necessary modifications described below to include the carbonate system), and ERSEM is planned to be used. The remaining models are described briefly as there may be something to that can be incorporated, with regards to either the modelling approach or the inputs to the models.

ERGOM

Kuznetsov and Neumann (2013) added a carbon cycle model to ERGOM by including two additional state variables, DIC and A_T, and ran this with MOM3.1 for the Baltic Sea. They implemented A_T as a passive tracer. This may be sufficient for the Baltic, since calcifying organisms are virtually absent in the Baltic Sea, but this aspect would need to be developed in order to use this model for other European Regional Seas. They introduced DIC using the Redfield C:N:P ratio (106:16:1), and included a sink due to primary production, sources due to mineralization of dead organic material (in the water column and in sediments) and respiration and excretion of phytoplankton and zooplankton.

The modifications made by Kuznetsov and Neumann (2013) would need to be further developed to be used in any of the other European Seas since some of the assumptions made for the Baltic Sea would not be valid elsewhere. The development required is not trivial and would require time resource and either a person with a background in modelling ocean acidification or significant training for a present member of the ecosystem modelling group. One other issue is that the present ERGOM setup is for the Mediterranean Sea. Due to the severe lack of data for this region (see below), this is unlikely to be a good test case for incorporating the carbonate system into ecosystem models.

ERSEM

A series of modelling studies have been carried out by modifying ERSEM to include the carbonate chemistry, and the Marine Ecosystem Evolution in a Changing Environment (MEECE) project outlines a method for doing this (see (http://www.meece.eu/documents/deliverables/wp2/d2.2.pdf). MEECE developed a set of FORTRAN subroutines that calculate the carbonate system at any given point in marine space time, given values for temperature, salinity, DIC and depth (pressure). The inclusion of the carbonate system is based on HALTAFALL (Ingri *et al.*, 1967), an iterative chemical speciation model which has been applied (Artioli *et al.*, 2012; Blackford *et al.*, 2008; Blackford and Gilbert, 2007)} to use calculated dissolved inorganic carbon (a state variable in ERSEM) and parameterized total alkalinity to derive pH and the partial pressure of CO_2 in the water. However, so far there is no feedback between the altered CO_2, pH and the ecosystem processes included in ERSEM. Output values are: total alkalinity, pH, pCO_2, carbonate and bicarbonate ion concentrations, and calcite and aragonite calcification states.

Partial pressure of CO_2 in the water drives the air-sea flux calculation on CO_2 using the parameterization of Nightingale *et al.* (2000). Blackford *et al.* (2008) forced their model assuming a constant atmospheric CO_2 concentration of 375 ppm, riverine DIC inputs derived from Pätsch and Lenhard (2004) and Thomas *et al.* (2005b), and an assumption of zero flux divergence for DIC at the lateral boundaries. Artioli *et al.* (2012) extended this model setup to include a parameterization for alkalinity that explicitly accounts for riverine inputs and

the influence of biological processes. Their model showed good to reasonable agreement for the physical (temperature and salinity), biogeochemical (nutrients) and carbonate system (DIC and A_T) variables, but found that uncertainly in riverine forcing and primary production led to unsatisfactory derivation of the derived variables (pH and pCO_2). They found that the high nonlinearity of the CO_2 system can imply very high uncertainty in air-sea fluxes as well as in simulating the impact of ocean acidification on primary production. This uncertainty would need to be reduced in order to examine the imps=acts of ocean acidification on ecosystem functions.

MEDUSA, Model of Ecosystem Dynamics, nutrient Utilisation, Sequestration and Acidification

MEDUSA (Yool *et al.*, 2011, 2013) is an ecosystem model developed as part of the NERC Oceans 2025 programme. It is embedded within NEMO and uses nitrogen as its main 'currency', but also includes silicon and iron (Figure 2). It is currently being used as part of ROAM, the regional seas modelling component of NERC's Ocean Acidification programme (UKOARP) and as a participating model in the EURO-BASIN project to study anthropogenic impacts on ecosystem function.

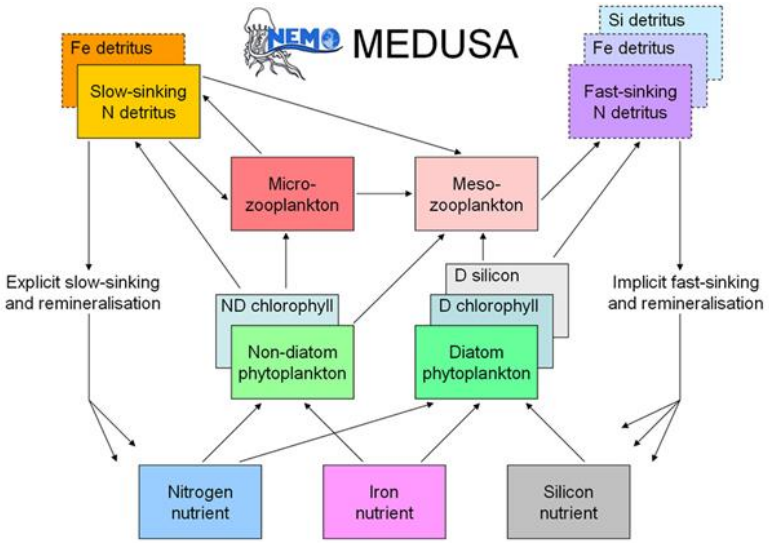

Figure 2: schematic of MEDUSA, from http://noc.ac.uk/science-technology/research-groups/msm/biogeochemical-modelling

The latest version of the model (Yool *et al.*, 2013) includes state variables for DIC, alkalinity, dissolved oxygen and detrital carbon (permitting variable C:N in exported organic matter), as well as a simple benthic formulation and extended parameterisations of phytoplankton growth and detritus remineralisation. For the air-sea gas exchange they use the same numerical scheme published by Blackford and Gilbert (2007) and used in Artioli *et al.* (2012). They implement a simply modelled cycle of alkalinity with three terms: one for $CaCO_3$ production, and one each of pelagic and benthic dissolution. So far this model has only been validated on the global scale, so its suitability for investigating the regional impacts of ocean acidification remains untested.

MIRO&CO-3D

MIRO&CO-3D (Gypens *et al.*, 2004, 2009, 2011) is a coupling of the biogeochemical MIRO model with the physicochemical module of Hannon *et al.* (2001) that describes the seawater carbonate system and air-sea CO_2 exchange. The Hannon *et al.* (2001) seawater carbonate chemistry module adds two state variables, DIC and A_T, for the description of the carbonate system in seawater and the evaluation of the exchange of CO_2 across the air-sea interface. The speciation of the carbonate system (pCO_2 and pH) is calculated from DIC and A_T, using the carbonic acid dissociation constants given by Mehrbach (1973), the boric acid dissociation constant given by Dickson (1990), and the CO_2 solubility coefficient given by Weiss (1974). The saturation state of Ω_{ca} and Ω_{ar} are computed from simulated surface pCO_2, A_T, sea surface salinity (SSS) and SST, using the calcite and aragonite solubility given by Mucci (1983). Air-sea CO_2 fluxes are calculated from the pCO_2 gradient across the air-sea interface and the gas transfer velocity parameterization as a function of wind speed of Nightingale *et al.* (2000).

Considerations of using these existing models

Some of the above-mentioned models lend themselves more readily than others to the current modelling work being carried out within the Water Resources Unit at JRC. The trait-based self-assembling modelling approach used by Follows *et al.* (2007) could be a way to describe adaptation within a model, one of the issues with using functional type models.

However, an exhaustive quantitative comparison against field observations has not been performed for such models (in particular they have only been used at global scales and their suitability for regional scale studies is not clear), and there are parameterisation problems in terms of the rule choices for the energetic and metabolic trade-offs. Developing this sort of modelling would require a specialist dedicated to developing such models for shelf seas with significant time to carry out the necessary development.

In order to use the FORTRAN routines developed for ERSEM, a validated GETM-ERSEM model is needed. This method of implementation of the HALTAFALL model, as described by Blackford *et al.* (2009) will not work with ERGOM, the biogeochemical model currently used at JRC since it requires the declaration of DIC as a state variable. A carbon cycle has been added to ERGOM by Kuznetsov and Neumann (2013), so this could potentially be developed for the JRC Mediterranean model. However, further development would be needed to that undertaken by Kuznetsov and Neumann (2013) as they introduced total alkalinity as a passive tracer, whereas various biogeochemical processes such as uptake of nutrients during primary production, denitrification, nitrification, sulfate reduction, sulfide oxidation and other influence total alkalinity (Wolf-Gladrow *et al.*, 2007).

Attempts by other groups at running ocean acidification models (Blackford and Gilbert, 2007; Artioli *et al.*, 2012; Kuznetsov and Neumann, 2013) have highlighted the need to improve the treatment of coastal processes such as river loads, optical properties and parameterisation of A_T. There is still significant development needed in order for regional sea models to be able to examine the effects of ocean acidification on ecosystem function and thereby identify the economic and social impacts. There is a lack of observations of basic carbonate parameters across the shelf seas, and high-frequency sampling at time series stations is needed. Some of these issues are explored further below.

Calculation of total alkalinity

Alkalinity, A_T is determined by the concentration of strong ions (such as Ca^{2+}) in the water (Zeebe and Wolf-Gladrow, 2001). This is not directly dependent upon pH, but determined by freshwater fluxes, riverine inputs, fluxes to and from sediment and biological

transformations. In ocean models, surface A_T is either specified – as a constant value or empirically determined function of salinity (following Millero *et al.*, 1998, or Lee *et al.*, 2006) – or it can be a prognostic variable influenced by freshwater fluxes and biological cycling of calcium and nitrate (Follows *et al.*, 2006).

Kuznetsov and Neumann (2013) represented A_T as a passive tracer, but this is only appropriate for regions where calcifying organisms are virtually absent. For open ocean situations the derivation of alkalinity from modelled salinity is robust (Millero *et al.*, 1998; Lee *et al.*, 2006). However, this relationship is at best highly approximate in shelf seas where the linear relationships with salinity break down (Thomas *et al.*, 2009) and biological activity can also significantly alter in-situ alkalinity (Blackford *et al.*, 2009) through processes such as calcium carbonate precipitation or production of particulate organic matter by microalgae (Wolf-Gladrow *et al.*, 2007).

Blackford and Gilbert (2007) parameterized the total alkalinity from salinity fields. They used two linear regressions, one with a positive slope for salinity higher than 34.65 (from Bellerby *et al.*, 2005), and one with negative slope to take account of riverine discharge of alkalinity (derived from Dutch coast data, Borges and Frankignoulle, 1999). This parameterisation is crude as it treats the entire coastal area using a single statistical relation derived from an area influenced by a river with high alkalinity. Furthermore it does not consider how changes in nutrient concentration affect A_T, thereby underestimating the variability.

Artioli *et al.* (2012) used the coupled model POLCOMS-ERSEM in the North Western European Shelf with a new parameterization for alkalinity that explicitly accounts for riverine inputs and the influence of biological processes. They divided the calculation of A_T into two components. Firstly a diagnostic component representing the oceanic contribution calculated using the standard regression between A_T and salinity for the Atlantic Ocean (Millero *et al.*, 1998). Secondly, a prognostic component that is fully advected and diffused by the circulation model that simulates the variability of A_T due to riverine inputs and all the biogeochemical processes influencing nutrients. Their model showed good to reasonable agreement for the principal variables, physical (temperature and salinity), biogeochemical

(nutrients) and carbonate system (dissolved inorganic carbon and total alkalinity), but did not yet simulate the derived variables, pH and pCO2, satisfactorily.

Blackford *et al.* (2009) suggest that the ideal approach for shelf systems is to describe alkalinity as a separate state variable which takes the form of a function of background alkalinity, riverine alkalinity nutrient processes and the mineralization and dissolution of calcium carbonate. Up to now most modelling studies have only included a parameterisation of A_T. Yool *et al.* (2013) have added a simple alkalinity cycle to their biogeochemical model, so perhaps this method could be extended to either ERGOM or ERSEM. The improvement of the treatment of A_T in these models is clearly key to the successful representation of the carbonate cycle.

Nutrient speciation and nitrification parameterisation

Nutrient speciation shows defined shifts with changes in pH (Zeebe and Wolf-Gladrow, 2001), for example, both the proportion of NH_3 (to NH_4^+) and that of PO_4^{3-} (to HPO_4^{2-}) are very sensitive to small variation in pH. It has been shown that nitrification rates will drop with decreasing pH (Huesemann *et al.*, 2002), and there is evidence that this can affect nutrient speciation in marine systems over CO_2 concentrations relevant to ocean acidification (Blackford and Gilbert, 2007). This will result various marine ecosystem disturbances such as changes in phytoplankton community structures and potential eutrophication phenomena.

The effect of pH on nitrification can be parameterised from Huesemann *et al.* (2002), for example, Blackford and Gilbert (2007) adopted this. However, the Huesemann et al. (2002)} parameterisation describes only one impact on the nitrogen cycle, whereas other parts of the nitrogen cycle are known to be sensitive. Nitrogen fixation has been shown to increase significantly at elevated CO2 in *Trichodesmiun* (Hutchins *et al.*, 2007) and benthic-pelagic fluxes of nutrients are sensitive to pH (Widdicombe and Needham, 2007). These processes are not yet included in the models used so far.

Nevertheless, Blackford (2010) highlights the importance of a variable carbon to nutrient stoichiometry and a consideration of microbial controls and process to investigate the carbon cycle in shelf sea regions. This suggests that the modifications made by Kuznetsov and Neumann (2013) to include DIC in the ERGOM model may not be sufficient. If the ERGOM model is chosen for ocean acidification scenarios, then further model development will be necessary to include a variable carbon to nutrient stoichiometry. This could perhaps follow the methods used by Yool *et al.* (2013) in the development of the MEDUSA model.

Riverine inputs

Riverine input of dissolved inorganic carbon and alkalinity is poorly monitored but significant in, for example, coastal regions of the North Sea (Thomas *et al.*, 2005b; Pätsch and Lenhard, 2004; Seitzinger *et al.*, 2005). Gypens *et al.* (2011) showed that riverine DIC and nutrients can contribute to a decrease in pH of about 0.2, depending on scenarios of river discharge. Riverine alkalinity can also vary greatly due to changing patterns of rainfall and land use: for example, the alkalinity of the Mississippi has increased by more than 50 % over the last half century (Raymond and Cole, 2003). Climate change predictions indicate the high probability of changes to regional rainfall patterns which, alongside changes in land use and industrial processes will modify fluvial inputs to coastal systems, affecting nutrients, optical properties, inorganic carbon and alkalinity (Raymond and Cole, 2003; Gypens *et al.*, 2009), potentially masking or exacerbating the atmospheric effect (Borges and Gypens, 2010). Riverine inputs are not routinely monitored and this is an issue that will contribute greatly to model uncertainty.

Data issues

The performance of any model must be verified and experimental results are essential for parameterising model ecosystem responses. The dynamics of DIC in the marine systems are a combination of physical processes, carbonate chemistry and biological processes each operating on different scales. However, observational data sets that characterize this range are rare (Blackford, 2010). The available data sets are summarised below:

1. The Global Data Analysis Project (GLODAP, http://cdiac.ornl.gov/oceans/glodap/Glodap_home.htm, Key *et al.*, 2004) has brought together inorganic carbon data collected on cruises of the World Ocean Circulation Experiment, the Joint Global Ocean Flus Study, and the Ocean Atmosphere Carbon Exchange Study. The data is available as either bottle data or gridded data. The gridded dataset consists of global grids with 1˚ horizontal resolution, interpolated onto 33 depth intervals from the surface to 5500 m.
2. The Lamont-Doherty Earth Observatory (LDEO, http://www.ldeo.columbia.edu/res/pi/CO2/carbondioxide/pages/pCO2data.html) pCO_2 dataset collects surface water pCO_2 measurements made since the 1970s. These are not consistent in space and time
3. The CANOBA project (CArbon and nutrient cycling in the NOrth Sea and the BAltic sea) provides a dataset for 3D model validation over a seasonal cycle. It includes vertically resolved measure of physical (temperature, salinity) and chemical (nutrients, dissolved oxygen, DIC, A_T, and pH) variables repeated seasonally in a set of stations spread over the entire North Sea from summer 2001 to spring 2002.
4. The Ferrybox project collects data from the P&O ferry Pride of Bilbao, which runs between Portsmouth (UK) and Bilbao (Spain). The project has been measuring the carbonate chemistry along this route for several years.
5. Carbonate chemistry data for the Mediterranean Sea and Black Sea are scarce. The DYFAMED (DYnamique des Flux Atmosphériques en MEDiterranée) time series station is located in the Western Mediterranean basin and data collected between 1991 and 2007 (including alkalinity and pCO2) can be accessed at: http://www.obs-vlfr.fr/dyfBase/

There are some satellite-derived products for monitoring chemical changes in seawater (Sun *et al.*, 2012 including air-sea flux, particulate inorganic carbon (PIC), particulate organic carbon (POC), A_T and calcification rate. The National Oceanic and Atmospheric Administration (NOAA) Coral Reef Watch and Atlantic Oceanographic and Meteorological Laboratory have developed the Experimental Ocean Acidification Product Suite (OAPS) to provide synoptic estimate of sea surface carbonate chemistry in the Greater Caribbean Region (http://coralreefwatch.noaa.gov/satellite/oa/index.php). This is a useful attempt to

observe ocean acidification with remotely sensed data. However there are still issues with the algorithms and low spatial resolution of these sorts of products. Satellite data are not yet suitable for use as model validation data sets.

In addition to the 'usual' data issues, such as data availability and spatial and temporal scale mismatches, there is also the potential for mismatch between the generally accepted theoretical derivations of the carbonate system as used in models and 'over-constrained' data sets. Theoretically, any pair of the four variables of the carbonate system (DIC, A_T, pH pCO_2) can be used to derive the others, but over-constrained carbonate system data sets have shown significant discrepancies when observed valued have been compared with derived values calculated from a subset of the measured variables (Hoppe *et al.*, 2011, Millero *et al.*, 2002}. Consequently, for example, pH derived from observed DIC and A_T may differ significantly from directly observed pH, which places limitations on the model. Depending on the pair of master variables used by the model system (usually DIC and A_T), the uncertainty in the other two (usually pH and pCO_2) will be larger.

Discussion

The impact of ocean acidification on biogeochemistry and biodiversity and subsequent feedbacks on climate will depend on the rate and magnitude of changes in ocean chemistry, so it is important to consider different scenarios of future CO_2 emissions to give useful projections and advice to policy makers. Modelling lends itself to this type of research and projections of future conditions and likely impacts must rely heavily on models that are designed to address ocean acidification research issues. Models will need to be used to understand the future chemical environment of pH and carbonate saturation states as a function of changes in factors such as atmospheric CO_2 concentrations, temperature and its effects on ocean circulation and mixing, and chemical interactions with sediments. On a different scale, modelling must also be used to examine the complex interactions between organism responses to environmental changes and the way in which these responses propagate up the marine food web. Since different ecosystems and regions are expected to be affected differently by ocean acidification, models will need to be targeted to specific

regions, taking into account each region's physical, chemical and ecosystem features in order to make meaningful projections of potential impacts.

Prediction of the carbonate system response is reasonably robust at a global scale (for example, Caldeira and Wickett, 2003; Orr *et al.*, 2005), but predicting the response of ecosystems and resources is problematic and is at a very early stage, particularly for shelf and marginal seas with high biological activity (for example, Blackford and Gilbert, 2007; Bourret *et al.*, 2007; Artioli *et al.*, 2012). This is partly due to the complexity of system drivers and partly to the range of effects identified and the variety of responses of different species. Model representation of the carbonate system in such complex environments is still in the early stages of development. Therefore, a translation of results into policy poses several problems for modellers.

The prediction of evolving carbonate chemistry in shelf and other marginal seas, in particular those which have high biological activity, close coupled benthic systems, complex physics and significant terrestrially derived inputs is a major challenge. Due to a range of natural physical and biological processes, riverine inputs, boundary conditions and runoff, natural variability of dissolved CO2 in seawater and related factors such as pH is relatively high in the European regional seas. Some species, calcifying or not, have the capacity to adapt to such conditions, others do not. Establishing the biological impacts of ocean acidification is then more difficult due to a range of physiological and ecological trade-offs leading to a variety of organism responses.

However, in order to adequately model acidification processes in regional seas, there is a need for a better quantification of the marine carbonate system and oceanic CO_2 uptake in specific locations, on seasonal, interannual and even longer time scales. Links with groups that are measuring this would be key in order to adequately model these processes. The Ocean Acidification International Coordination Centre (OA-ICC) Global Ocean Acidification Observing Network (GOA-ON) is coordinating a worldwide network for ocean acidification observations, including spatially and temporally resolved biogeochemical data for use in parameterizing and validating models. Interaction and cooperation with such a community

would be essential, as model development will be highly dependent on access to measurements and current knowledge and understanding of acidification processes.

There is clearly a lack of data for model calibration and verification in many of the European Seas, so uncertainty in model performance is likely to be large. A significant amount of model development is required and there are no existing model formulations that can be added to the current models used in the Water Resources Unit. The major challenges include the prediction of evolving carbonate chemistry in shelf and other marginal seas, in particular those which have high biological activity, close coupled benthic systems, complex physics and significant terrestrially derived inputs, and quantifying feedbacks, given the high degree of variability revealed by experimental studies and the potential for acclimation and adaption. Incorporating the carbonate system in the regional sea models will be a challenge and requires dedicated development time and collaboration with ocean acidification experts.

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Abstract

Given specific CO2 emission scenarios, predictions of future ocean carbonate chemistry are relatively certain at the global scale. However future regional ocean acidification and ocean carbonate chemistry are less well understood. A major challenge is assessing the risk of ocean acidification on marine food webs, ecosystems and ocean biogeochemistry.

Due to a range of natural physical and biological processes, riverine inputs, boundary conditions and runoff, the natural variability of dissolved CO2 in sea water is relatively high in regional seas. Some species, calcifying or not, have the capacity to adapt to such conditions, others do not. Establishing the biological impacts of ocean acidification is difficult due to a range of physiological and ecological trade-offs. Including the carbonate system in such complicated regions is a challenge, and significant development will be required to model this in regional seas.

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